

SYNTHESIS OF C₅ ETHERS FROM METHANOL AND 2-METHYL-1-PROPANOL (ISOBUTANOL)

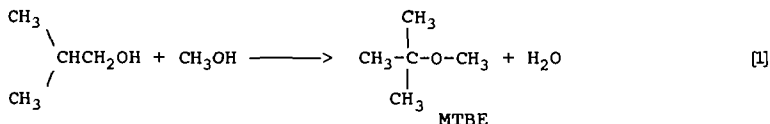
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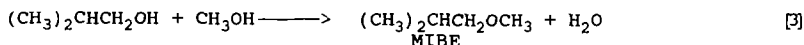
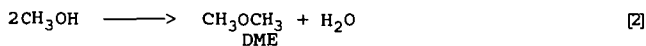
Introduction

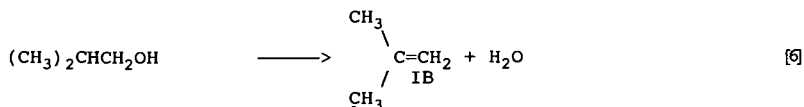
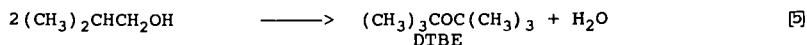
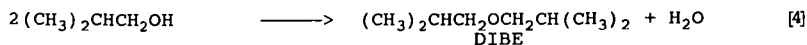
Methyl-tertbutyl ether (MTBE) and tertamyl-methyl ether (TAME) technology is well established with methanol and a branched olefin (iso-butene or 2-methyl-butene) as source feedstock (1,2). The recently announced engineering innovation of reaction with distillation led to a new process, ETHERMAX, by Dow-Hölse-Kohl (3), in which the thermodynamic equilibrium is shifted in favor of MTBE by the product removal directly in the catalytic reactor. Despite the very fast growth of the MTBE and TAME production capacity worldwide, there is a potential shortage of the feedstock olefins (4) and by some accounts of methanol (5), should MTBE/TAME be used as the principal oxygen additive and octane booster for partial replacement of aromatics in gasolines (3).

As isobutene can be obtained by dehydration of 2-methyl-1-propanol (isobutanol) and isobutanol can be directly synthesized from the syngas CO/H₂ (6,7), there is an alternative route to MTBE via the syngas-derived isobutanol. Still a more attractive route to MTBE would be via the direct coupling of alcohols,



if the selectivity of the process could be controlled so that reaction [1] is the dominant route. There are several other reactions that can occur in a system that couples isobutanol with methanol: coupling of two methanol molecules to dimethyl ether (DME) [2], of methanol and isobutanol to methyl-isobutyl ether (MIBE) [3] which is a low octane isomer of MTBE, of two isobutanol molecules to di-isobutyl ether (DIBE) [4] or di-tertbutyl ether (DTBE) [5], dehydration of isobutanol to isobutene (IB) [6], and oligomerization of isobutene to C₈, C₁₂, etc. hydrocarbons.

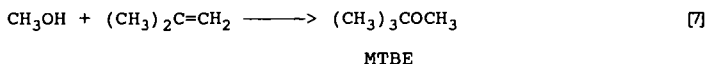




All of the above reactions [1] - [6] are acid-catalyzed, and the use of solid acids is preferred to that of acid solutions. The factors influencing selectivity are thermodynamic constraints, the concentration and strength of the catalyst acid sites, and mass transfer related phenomena such as shape- or diffusion controlled selectivity in zeolites. In this work we report on the selectivities of isobutanol-methanol coupling over two classes of catalysts, organic polymeric sulfonic acids and inorganic acids based on silica-alumina, mordenite, montmorillonite, and sulfate-modified zirconia.

Thermodynamic Considerations

The standard free energies for the key reactions involved in the set [1] - [6] are represented in Figure 1 for two temperatures, 298 and 400K. It is evident that at 400K and above, the synthesis of MTBE from methanol and isobutene [7]



becomes a thermodynamically uphill process while if the two alcohols are the reactants in reaction [1], the path to MTBE is exoenergetic. Further, the mixed ether isomer of MTBE, MIBE, that is readily formed over Nafion H (8), is a thermodynamically less favorable product than MTBE. Elevated pressure will favor the ether-forming reactions [1] - [5] over the dehydration of isobutanol [6] in which the molar volume increases when going from the left to the right.

Kinetic Considerations

Although kinetics of reactions [1] - [6] and related processes have been studied in detail only over Nafion H (9), it is important to summarize the main features of that kinetic behavior here, because the kinetic patterns provide guidelines for testing protocol over a wide range of catalysts. The results of kinetic studies of coupling methanol with isobutanol over Nafion H yield the following conclusions:

- (i) Dehydration of isobutanol to IB, reaction [6], requires two acid sites, one of which binds isobutanol and one that supplies an acid catalyzing function for the isobutanol dehydration. The consequence of this kinetic behavior is that at high pressures, isobutanol poisons its own

- dehydration and the kinetic order becomes negative with isobutanol concentration. Methanol also exhibits a retarding effect on isobutanol dehydration by competitive adsorption and blocking of the acid sites.
- (ii) The formation of DME, reaction [2], and DIBE, reaction [4], requires two sites occupied by the respective alcohol, methanol for DME and isobutanol for DIBE. The consequence of this behavior is that at high pressures, the kinetics become "saturated" and the rates of DME or DIBE reach constant values.
 - (iii) The formation of MIBE, reaction [3], requires two sites occupied by the two different alcohols. The consequence of this behavior is that there is a maximum rate at an optimum ratio of partial pressures of the two alcohols. Quantitative evaluation of the observed rates shows that isobutanol is approximately two times more strongly held by the acid sites of Nafion H than methanol.
 - (iv) The conversion of MIBE to the thermodynamically more stable MTBE or isobutene and methanol is kinetically strongly hindered.

The dual site character of all catalyzed reactions involved imposes a requirement that the acid sites be highly concentrated on the surface of any prospective heterogeneous catalyst. Further, pressure is recognized as an important variable controlling the selectivity to ethers (high pressures) or isobutene (low pressures).

Organic Polymeric Catalysts

In this section, we compare the outcome of isobutanol-methanol coupling under standard test conditions developed in this laboratory. Reaction conditions were similar to those described in Nunan et al (8). The test reaction used 5 g of catalyst at 90°C under a total pressure of 1 atm. The flow rate of each alcohol was 1.72 mol/kg cat/hr and was achieved by pumping an equimolar mixture of isobutanol and methanol. The flow rate of He and N₂ is 16 mol/kg cat/hr. The catalyst bed was diluted to 20 cm³ with Pyrex beads. The organic polymers were all sulfonic derivatives in their hydrogen form, and they are listed in Table I.

Steady state conversions were obtained within the first hour of the reaction. Data were collected for several hours time-on-stream during which no catalyst deactivation was detected. The results of the standard test over these polymers are summarized in Table II. The major products, excluding water, of the reaction of the two alcohols are given in this table. In addition, minor amounts of C₈ and C₁₂ hydrocarbons, formed from the di- and trimerization of isobutene, were detected. The order of activity of the catalyst was found to be Amberlyst ≈ Purolite > BioRad > Nafion.

Product selectivities for the different catalysts are illustrated by Figure 2. Water, which is, of course, the major product of these dehydration reactions, is not included in the selectivity analysis. Under the standard reaction conditions, Nafion-H appears to be the best catalyst for MIBE production. The other catalysts produce significant amounts of MTBE, along with other ethers, viz. DTBE, DIBE, and DME. The higher selectivity of Nafion towards MIBE formation may be due to the distinctly different nature

of the acid sites of Nafion. The sulfonic acid groups of perfluorinated Nafion contrast with the sulfonic acid groups of the other hydrocarbon based resins tested in this study.

Inorganic Solid Acid Catalysts

The following inorganic acid catalysts were tested: H-Mordenite (Norton), $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Davison), Montmorillonite K-10 (Aldrich), and ZrO_2 treated with sulfuric acid, which will be designated as ZrO_2/SO_4 .

The preparation of ZrO_2/SO_4 was according to the work of Hino and Arata (10). $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was added to aqueous ammonia to precipitate $\text{Zr}(\text{OH})_4$ which was washed and dried at 100 °C overnight. The dried $\text{Zr}(\text{OH})_4$ weighing 10 g was placed on a folded filter paper and 150 ml of 1N H_2SO_4 was poured through it. The wet powder was dried at 110°C overnight and then calcined at 620 °C for 3 hr. Pretreatment of other catalysts consisted of calcination of Mordenite and $\text{SiO}_2/\text{Al}_2\text{O}_3$ at 400°C, the Montmorillonite catalysts being used as received.

The reaction conditions and catalyst weight used for the inorganic catalysts were identical to those used for the organic catalysts mentioned above. In addition, in light of their much higher temperature stability, the inorganic catalysts were studied at reaction temperatures of 125°C, 150°C, 175°C, as well as 90°C.

The results of the standard test over these inorganic catalysts are summarized in Table IV.

The product selectivities of these catalysts are shown in Figures 3-6. Water, the coproduct of all the dehydration reactions, is not included in the selectivity calculations.

The patterns that emerge are the following:

- (i) H-mordenite is a selective catalyst for dehydration of methanol to DME. Isobutanol is not converted to any ethers or dehydrated significantly to isobutene over H-mordenite under the conditions used. Evidently the pore size or shape of H-mordenite restricts reactions of isobutanol; even though the isobutanol molecule is small enough to enter the larger channel pores of mordenite, its conversion is suppressed by one or all of the following three classic mechanisms of zeolite shape selectivity: (a) inaccessibility of acid centers that possibly reside primarily in the narrow side channels of the mordenite structure; this type of size exclusion in alcohol dehydration was first studied by Weisz et al. (11), however it should be noted that acid sites in mordenite are accessible to molecules as large as 1-methyl-2-ethylbenzene at higher temperatures (12) (b) retardation of isobutanol transport by preferential diffusion of methanol, diffusive selectivity was studied by Chen and Weisz (13) (c) size restrictions on the transition states involving isobutanol, isobutyl esters, and isobutyl oxonium ions. Csicsery first proposed the concept of restricted transition state selectivity in zeolites (12).

- (ii) Sulfate-modified zirconia is an efficient and highly selective catalyst for the dehydration of isobutanol to isobutene, with methanol dehydration to DME suppressed. The reasons for this selectivity pattern have not been established but it is tentatively suggested that isobutanol is more strongly bonded than methanol to the sulfate groups on the zirconia surface so that methanol activation is suppressed. The relative bonding strength of isobutanol and methanol to the sulfate-modified zirconia would have to be more markedly different than that on Nafion H because DME and MIBE are co-products with isobutene over Nafion H but not over the sulfate-modified zirconia.
- (iii) There is an overall order of activities for the dehydration reactions over the inorganic acids used,
 $\text{ZrO}_2/\text{SO}_4^{2-} > \text{H-mordenite} > \text{SiO}_2/\text{Al}_2\text{O}_3 > \text{H-Montmorillonite}$
- (iv) The inorganic catalysts are generally less active than the organic polymeric catalysts at 90°C except for H-mordenite which is active and selective for methanol dehydration to DME. Higher temperatures are needed for significant alcohol dehydration with inorganic catalysts. In general, the organic polymeric catalysts are unstable at these higher temperatures.

Conclusions

Acid-catalyzed reactions of an equimolar mixture of methanol and 2-methyl-1-propanol (isobutanol) gave rise to homo- and heteroethers, as well as to isobutene, depending on the catalyst used. The organic polymeric acids were selective towards MIBE which is a low octane isomer of MTBE. A particularly high selectivity to DME was displayed by H-mordenite, evidently due to a combination of factors that are summarily termed "shape selectivity". The sulfate-modified zirconia proved to be a selective catalyst for isobutanol dehydration to isobutene, with ether formation suppressed. The inorganic catalysts displayed a lower activity than sulfonated organic resins and thus higher temperatures were needed, but the sulfate-modified ZrO_2 has proven to be promising when isobutene is a desirable product of alcohol isobutanol dehydration in the mixture with methanol. The significant advantages of inorganic catalysts are their applicability at high temperatures and ease of regeneration.

Acknowledgements

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TABLE I
Organic Catalysts

	Polymer base	Resin type	Decomposition Temperature
Amberlyst-15	Polystyrene	Macroreticular	≈120 °C
Purolite 150	Polystyrene	Macroreticular	≈120 °C
BioRad AG50WX2	Polystyrene	Gel	≈120 °C
Nafion-H	Fluorocarbon	Gel	>200 °C

TABLE II
Yields over Organic Catalysts
(mol/kg cat/hr)

	DME	Butenes	MIBE	MTBE	C8 ether
Amberlyst-15	0.042	0.041	0.053	0.013	0.014
Purolite 150	0.034	0.048	0.062	0.011	0.015
BioRad AG50WX2	0.015	0.011	0.040	0.004	0.008
Nafion-H	0.004	0.002	0.014	0.0003	0.003

TABLE III
Yields over Inorganic Catalysts
(mol/kg cat/hr)

	T _{Reaction}	DME	Butenes	MIBE	MTBE	C8 ether
H-Mordenite	90°C	0.060	-----	-----	-----	-----
	125°C	0.6599	-----	-----	-----	-----
	150°C	0.83	0.068	-----	-----	0.004
ZrO ₂ /SO ₄ ⁼	90°C	-----	-----	0.003	-----	-----
	125°C	0.006	0.067	0.02	0.003	0.008
	150°C	0.027	0.696	0.068	0.009	0.017
	175°C	0.103	1.29	0.049	0.007	-----
SiO ₂ /Al ₂ O ₃	90°C	-----	-----	-----	-----	-----
	125°C	0.007	0.028	0.011	0.001	0.003
	150°C	0.021	0.225	0.032	0.005	0.014
	175°C	0.039	0.943	0.049	0.007	0.016
Montmorillonite	90°C	-----	-----	-----	-----	-----
	125°C	0.008	0.008	0.008	-----	0.004
	150°C	0.019	0.071	0.019	0.004	0.014
	175°C	0.034	0.378	0.029	0.014	0.031

Fig. 1 Free energy of ether synthesis reaction pathways

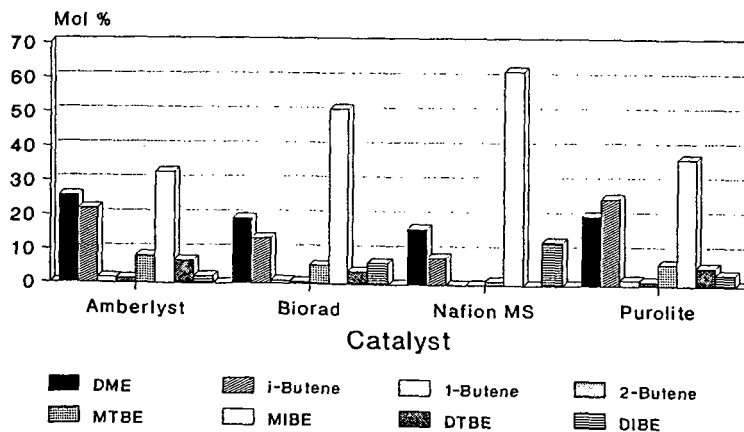
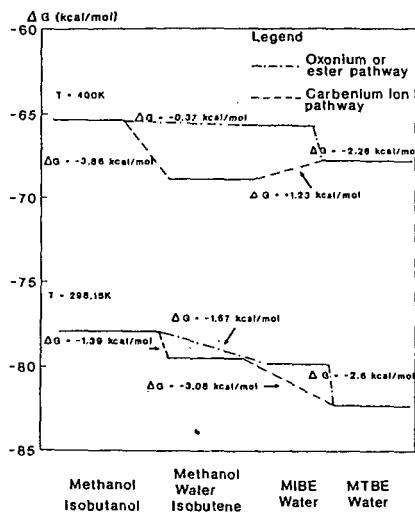


Fig. 2 Selectivity over organic catalysts for the methanol + isobutanol reaction at 90 °C.

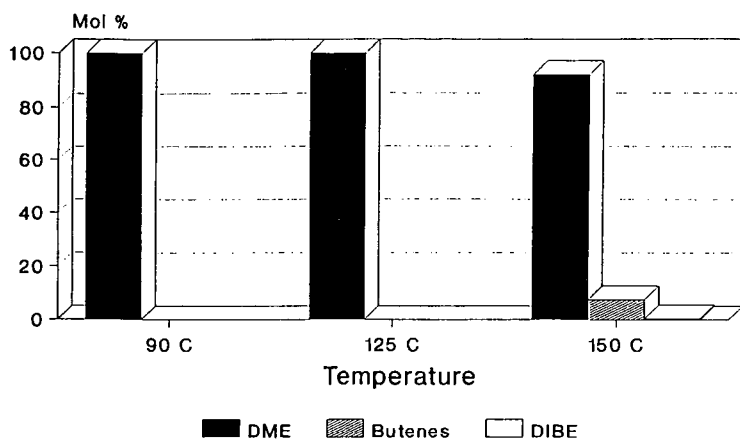


Fig. 3 Selectivity over H-mordenite for the methanol + isobutanol reaction at various temperatures.

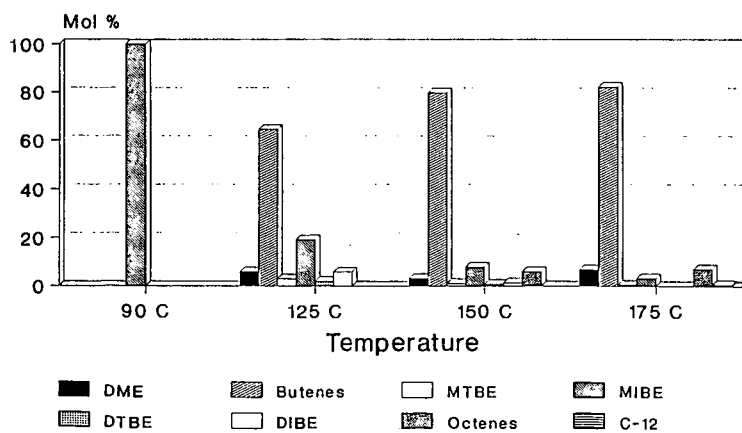


Fig. 4 Selectivity over ZrO₂/SO₄²⁻ for the methanol + isobutanol reaction at various temperatures.

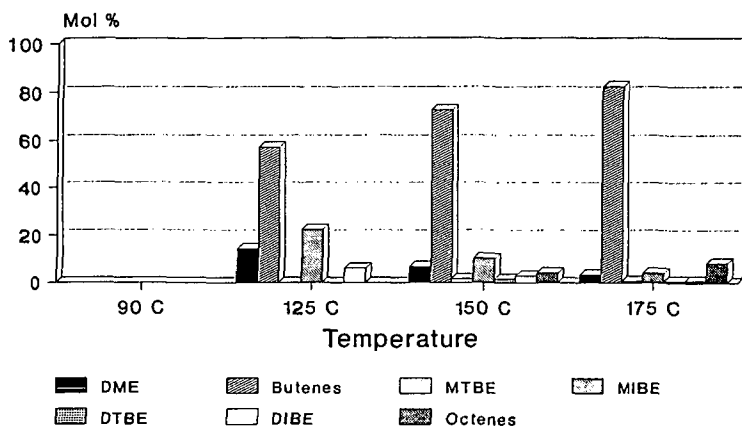


Fig. 5 Selectivity over $\text{SiO}_2/\text{Al}_2\text{O}_3$ for the methanol + isobutanol reaction at various temperatures.

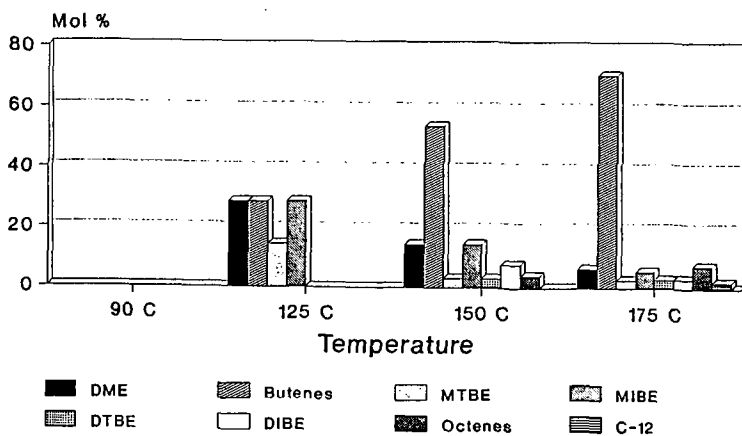


Fig. 6 Selectivity over Montmorillonite for the methanol + isobutanol reaction at various temperatures.